

AFWAL-TR-87-2042
Volume III

AD-A201 393

PRODUCTION OF JET FUELS FROM COAL DERIVED LIQUIDS

**VOL III - Jet Fuels Potential of Liquid By-Products From the
Great Plains Gasification Project**

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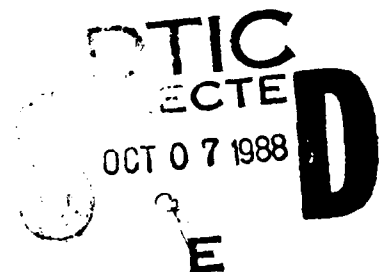
WESTERN RESEARCH INSTITUTE
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MAY 1988

INTERIM REPORT FOR THE PERIOD SEPTEMBER 1986 - DECEMBER 1987

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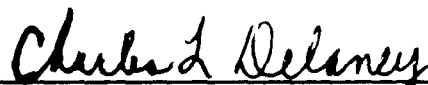
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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS None		
2a. SECURITY CLASSIFICATION AUTHORITY N/A			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A			5. MONITORING ORGANIZATION REPORT NUMBER(S) AFWAL-TR-87-2042, vol. III		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) N/A			7a. NAME OF MONITORING ORGANIZATION Air Force Wright Aeronautical Laboratories Aero Propulsion Laboratory (AFWAL/POSF)		
6a. NAME OF PERFORMING ORGANIZATION Western Research Institute		6b. OFFICE SYMBOL (If applicable)		7b. ADDRESS (City, State, and ZIP Code) Wright-Patterson Air Force Base, Ohio 45433-6563	
6c. ADDRESS (City, State, and ZIP Code) P.O. Box 3395 University Station Laramie, WY 82071		8a. NAME OF FUNDING/SPONSORING ORGANIZATION Air Force Aeronautical Laboratories		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER FY1455-86-N0658	
8b. OFFICE SYMBOL (If applicable) AFWAL/POSF		8c. ADDRESS (City, State, and ZIP Code) AFWAL/POSF Wright-Patterson AFB, OH 45433-6563		10. SOURCE OF FUNDING NUMBERS	
PROGRAM ELEMENT NO. 63215F		PROJECT NO. 2480		TASK NO. 16 WORK UNIT ACCESSION NO. 01	
11. TITLE (Include Security Classification) Production of Jet Fuels from Coal Derived Liquids--Vol. III, Jet Fuels Potential of Liquid By-Products from the Great Plains Gasification Project					
12. PERSONAL AUTHOR(S) E. B. Smith, F. D. Guffey, L. G. Nickerson					
13a. TYPE OF REPORT Interim		13b. TIME COVERED FROM Sept 86 TO Dec 87		14. DATE OF REPORT (Year, Month, Day) May 1988	
15. PAGE COUNT 45					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Jet Fuel, Turbine Fuel, JP-4, JP-8, Crude Phenol, Tar Oil, Naphtha, Great Plains Gasification Plant, Coal Liquids		
21	21	07			
04	05	03			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Three liquid by-products from the Great Plains Gasification Project, tar oil, crude phenols, and naphtha, were evaluated as potential sources of military jet fuels. Tar oil, produced at about 3200 barrels per day (BPD), is a highly aromatic lignite pyrolysis liquid with a typical density of 1.01 and boiling range of about 220-975°F (104-524°C). Crude phenols, extracted from process water at about 900 BPD, is essentially a mixture of phenols, cresols, dihydric phenols, and naphthols, with an oxygen content averaging over 13 wt %. The naphtha is a low-boiling mixture extracted from syngas at about 725 BPD. Chief components are benzene, alkyl-benzenes, sulfur compounds, and highly variable amounts of methanol, acetone, and methylethyl-ketone. Based on these typical by-product characteristics, preliminary assessments were that the tar oil was the most promising jet fuel source, that crude phenols was a questionable source because of its high oxygen content, and that naphtha was a poor source because of its low-boiling range. These assessments were confirmed by hydrogenation experiments which demonstrated that JP-4, JP-8, and high-density JP-8 could be prepared from tar oil at hydrogen consumption levels greater than 3400 standard cubic feet per barrel (scfb). It was also demon-					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL William E. Harrison, III			22b. TELEPHONE (Include Area Code) 513-255-6601		22c. OFFICE SYMBOL AFWAL/POSF

DD Form 1473, JUN 86

Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

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19. strated that crude phenols could make a minor contribution to JP-4 production, and that naphtha was unsuited to jet fuels production.

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SUMMARY

Three liquid by-products from the Great Plains Gasification Project--tar oil, crude phenols, and naphtha--were evaluated as potential sources of military jet fuels. Tar oil, produced at about 3,200 barrels per stream day (bpsd) is a highly aromatic lignite pyrolysis liquid with a typical density of about 1.01 and boiling range of about 220-975°F (104-524°C). Crude phenols, extracted from process water at about 900 bpsd, is essentially a mixture of phenol, cresols, dihydric phenols, and naphthols, with an oxygen content averaging over 13 wt %. The naphtha is a low-boiling mixture extracted from syngas at about 725 bpsd. Its chief components are benzene, alkylbenzenes, sulfur compounds, and highly variable amounts of methanol, acetone, and methylethylketone. Based on these typical by-product characteristics, preliminary assessments indicated that the tar oil was the most promising jet fuel source, crude phenols was a questionable source because of its high oxygen content, and naphtha was a poor source because of its low boiling range.

Each by-product was used as a feedstock for catalytic hydrogenation experiments to characterize its hydrogenation behavior and to determine the properties of intermediate products at various levels of process severity. Shell 424 Ni-Mo catalyst was employed in all experiments. Tar oil experiments were conducted at 2,000 psig, with liquid hourly space velocities (LHSV) of 1.00, 0.50, or 0.33, hydrogen feed ratios from 6,000 standard cubic feet per barrel (scfb) to 16,000 scfb, and at temperatures from 650°F (343°C) to 750°F (399°C). Phenols experiments were conducted at 2,000 psig, LHSV of 0.50 or 1.00, with a hydrogen feed ratio of 6,000 scfb and at temperatures ranging from 550°F (289°C) to 650°F (343°C). Naphtha experiments were conducted at 500 psig, with LHSV of 1.00, a hydrogen feed ratio of 1,500 scfb, and temperatures of 300°F (149°C) to 500°F (260°C).

Particulate matter in the whole tar oil caused catalyst bed plugging in initial experiments. This problem was solved by distilling the oil to reject the particulate matter in the distillation residue.

The tar was flash-distilled to produce two fractions boiling in the (nominal) ranges of IBP-450°F (IBP-232°C) and 450-750°F (232-299°C). Eight products were collected during hydrogenation of the heavy distillate. None of these were suitable as an intermediate for production of a specification-grade fuel sample, because of insufficient aromatics saturation.

The heavy distillate was found to be more resistant to saturation than the whole oil. The light distillate was extracted with caustic to remove cresylic acid components. The raffinate was blended with heavy distillate to yield a partially deoxygenated feedstock. This blend was employed in experiments conducted at more severe conditions than those previously employed.

Five products were collected, three of which were sufficiently saturated to serve as sources for preparation of test fuel samples. A JP-8 sample was prepared by distilling a blend of two of these products to the

typical specification boiling range. The distillate apparently met critical specification properties for grade JP-8. A JP-8X (experimental high-density) sample was prepared by distillation of a third product. This distillate met target specification properties for JP-8X except for the freezing point, which was too high. Calculations based on compound-class and boiling-range composition indicated that only the product generated at the most severe conditions (LHSV 0.33, 750°F [299°C]) could yield a specification-grade JP-4 distillate. These experiments indicate that the hydrogen consumption level to produce acceptable jet fuels from tar oil could exceed 3,500 standard cubic feet per barrel.

Experiments conducted with the crude phenols were intended to find the level of hydrogenation severity needed to eliminate oxygen in the product and to determine product properties. At the pressure and hydrogen feed ratio employed (2,000 psig, 6,000 scfb) the lowest temperature at which deoxygenated products were obtained was 600°F (316°C). At these conditions, measured hydrogen consumption levels were 4,400 scfb at LHSV of 1.00, and almost 5,000 scfb at LHSV of 0.50. The deoxygenated products were mostly paraffins and monocycloalkanes, 95 vol % of which distilled below 490°F (254°C). These high levels of hydrogen consumption, much of which is lost to water production, and the low boiling range of products indicate that the crude phenols by-product is not a good source for jet fuels, but could contribute to production of JP-4.

Hydrogenation of the naphtha, a low-boiling, highly aromatic, high-sulfur by-product, was conducted at low severity (500 psig, LHSV 1.0, 300-500°F [149-260°C]). The object was to identify conditions that would desulfurize the product while retaining high aromatics content. At 500°F (260°C), the measured hydrogen consumption was 660 scfb, the product contained 550 ppm sulfur and was composed of 58 wt % monocycloalkanes and 42 wt % light aromatics. More than 95 vol % of this product boiled below 300°F (149°C). The experiment demonstrated that the naphtha by-product is not a suitable source for jet fuel, but could be used as gasoline blend stock after hydrodesulfurization.

FOREWORD

In September 1986, the Fuels Branch of the Aero Propulsion Laboratory at Wright-Patterson Air Force Base, Ohio commenced an investigation of the potential for production of jet fuel from the liquid by-product streams produced by the gasification of lignite at the Great Plains Gasification Plant located in Beulah, North Dakota. Funding was provided to the Department of Energy (DOE) Morgantown Energy Technology Center (METC) to administer the experimental portion of this effort. This report details the effort of the Western Research Institute (WRI), who, as a contractor to DOE (DOE Contract Number DE-FC21-86MC11076), studied the potential of the liquid by-product streams for the production of jet fuels. DOE/METC was funded through Military Interdepartmental Purchase Request (MIPR) FY1455-86-N0658. Mr. William E. Harrison III was the Air Force Program Manager, Mr. James D. Westhoff was the DOE/METC Program Manager, and Mr. Edgar B. Smith was the WRI Program Manager.

The authors gratefully acknowledge the contributions of the following individuals: Mr. Bruce E. Thomas, Engineering Technician; and in particular Mrs. Jean C. Tweed, Administrative Secretary. The many helpful suggestions of Mr. William E. Harrison III, Air Force Program Manager and Dr. Warrack G. Willson, University of North Dakota Energy and Minerals Research Center were of great benefit throughout the contract program.

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SECTION I

INTRODUCTION

The Great Plains Gasification Plant (GPGP) near Beulah, North Dakota, gasifies 14,000 tons of lignite coal per day to produce about 145 MMscf/day of synthetic natural gas. In addition, the plant produces three liquid by-products--tar oil, crude phenols, and naphtha at nominal rates of 3,200, 915 and 725 barrels per stream day (bpsd), respectively. The gas is sold to several major distributors at a contract price of over five dollars per MMBtu, or more than double the current spot market price. The by-products are burned in plant boilers to generate steam for gasification and other plant requirements. For the life of the contracts, which expire in 1989, the GPGP may cover its operating costs by producing SNG alone; however, diversification of the product slate by upgrading by-products to produce chemicals or transportation fuels could give the plant more flexibility to earn a higher return on investment. This possibility is of considerable interest to the Department of Energy, the proprietor of GPGP since the 1985 withdrawal of private industry from the project. One prospective customer for upgraded by-product liquids is the U.S. Air Force.

Minot Air Force Base, about 90 miles from the plant, pays premium prices for aviation jet fuel, grade JP-4, because of the remote location of the base from domestic fuel sources. Fuel required for operating base aircraft (about 2,300 barrels per day) is delivered by truck. If it were shown that JP-4 could be produced from GPGP by-products at a competitive price, the Minot Air Force Base would represent a secure long-term market for the project. For these reasons, the Department of Energy and the Air Force share an interest in exploring the potential of GPGP by-products as a domestic source of jet fuel.

Typical inspection characteristics of GPGP by-products permit some speculation of their potential as sources of jet fuel or other high-value products. The naphtha boils in the gasoline range and is composed mainly of low-boiling aromatic hydrocarbons. It is probably too volatile and deficient in hydrogen to be a suitable source for jet fuel, and probably would have greater potential value, after minimal upgrading, as a petrochemical intermediate or as a gasoline blending component. The crude phenols represent a source of cresylic acids that could be extracted, or concentrated by distillation to an endpoint of about 450°F (232°C). The entire tar oil stream combined with the higher-boiling portion of the phenols, totaling more than 3,000 bpsd, could represent feedstock for an upgrading process unit to supply the daily JP-4 requirement for Minot AFB. Hydrocracking could be the process unit of choice, because of its well-demonstrated flexibility to produce a variety of fuel slates. This flexibility would permit the plant to produce other fuels such as JP-8, a kerosene-type fuel which will eventually supplant JP-4, or Jet A-1, the commercial counterpart of JP-8. High-density fuel is another type in the development stage for which these highly aromatic coal-derived liquids could be an excellent source.

Development of a technology base for production of coal-derived JP-4 and JP-8 paves the way for long-term development of coal-derived fuels of considerably higher density than current conventional fuels. Such high-density jet fuels could significantly increase the range of volume-limited aircraft. Prototype high-density jet fuels are mixtures of cyclic hydrocarbons which will probably have higher aromatics content than the maximum permitted by current jet fuel specifications. It can therefore be predicted that a coal liquid such as the highly aromatic GPGP tar oil could be a choice feedstock for production of high-density fuels.

Based on these observations, the principal objective of this study was to quickly develop data base information on the overall potential of Great Plains by-product coal liquids for production of military jet fuels. With three fuel grades in mind, JP-4, JP-8 and a high-density fuel designated JP-8X, this investigation had the following goals:

1. to perform detailed analyses of GPGP by-product liquids in order to evaluate them as feedstocks for jet fuel production;
2. to characterize the processing behavior of the by-products by performing a series of catalytic hydrogenation screening experiments on each by-product, or portions or mixtures of them;
3. to perform detailed analyses of hydrogenation products in order to evaluate them as process intermediates for fuels production;
4. to relate process conditions to product composition.

Some critical properties of the three types of jet fuel of primary interest in this investigation are found in Table 1. Properties listed for grades JP-4 and JP-8 are from current specifications (reference 1). Properties for JP-8X are target values for a fuel type still in the development stage.

Table 1. Critical Properties of USAF Turbine Fuels

Property	JP-4	JP-8	Near-Term JP-8X
Specific Gravity, 60/60°F	0.71-0.802	0.788-0.845	0.850 min
Hydrogen, wt %	13.6 min	13.5 min	12.8 min
Boiling Range, °F	Report-608	Report-626	300-653
ΔH_c , Net Btu/gal $\times 10^{-3}$	Not specified	120.9 min	128 min
Freezing Point, °F	-72 max	-58 max	-47 max
Aromatics, vol %	25.0 max	25.0 max	30.0 max
Paraffins, vol %	Not specified	Not specified	0-10

SECTION II

ANALYSIS OF GREAT PLAINS BY-PRODUCT LIQUIDS

Two drums of tar oil, two drums of crude phenols, and one drum of naphtha were supplied by the Air Force Aero Propulsion Laboratory (APL) for this study. The sample numbers designated for these products are as follows: tar oil, REF 86-72A and REF 86-72B; crude phenols, REF 86-73A and REF 86-73B; naphtha, REF 86-74. Inspection analyses on the two drums of tar oil showed sufficient similarity that REF 86-72A was selected for this study with REF 86-72B held in reserve. Inspection analyses were also similar for the two drums of crude phenols, and REF 86-73A was selected for this study with REF 86-73B held in reserve.

1. TAR OIL ANALYSIS

Samples of each drum of tar oil were analyzed for bulk properties. In addition, a portion of REF 86-72A tar oil was filtered through a Balston filter cartridge and the filtrate submitted for analysis as sample REF 86-72AF. Analytical results are listed in Table 2. Also listed for comparison are average tar oil analytical values provided by ANG Coal Gasification Company, operators of the Great Plains plant (reference 2). In general, Western Research Institute (WRI) samples were found to have slightly higher densities, lower water contents, lower carbon contents and higher oxygen contents than average reported values. ASTM D-2887 (simulated distillation) results are in fairly good agreement with the results of true-boiling point (TBP) distillation. ASTM D-86 distillation values compare very poorly with average values. The D-86 distillation conducted on REF 86-72A was extremely troublesome because of the water in the sample, which caused frothing at the initial boiling point, and because the distillate tended to freeze in the condenser after about 40 vol % recovery. At 87 vol % recovery the residual oil cracked. The ASTM D-2887 correlation values shown in lieu of D-86 values for REF 86-72B compare poorly with both the average D-86 values and with the values determined by our ASTM D-86 distillation of REF 86-72A. We concluded that the ASTM D-86 distillation method is not particularly useful for comparing GPGP tar oils.

Tar bases and tar acids were isolated from a 10-g sample of tar oil by sequential liquid-liquid extraction with aqueous 2 N hydrochloric acid solution and aqueous sodium hydroxide solution. The neutral raffinate fraction was separated into compound-type concentrates by chromatography on neutral alumina and on silica gel/silver nitrate. Because of the many different degrees of alkyl substitution, there was a considerable overlap in elution order for some compound types that necessitated another separation on short silica gel columns to achieve an acceptable degree of integrity in these fractions. The individual subfractions were dissolved in methylene chloride and analyzed by infrared spectroscopy in the absorbance mode.

The results of separation of tar oil by liquid-liquid extraction and further chromatographic separation of the neutral oil into subfractions are listed in Table 3. The value for tar acids, 19.8 wt %, is considerably higher than typical tar-acid values from ANG data, which

Table 2. Bulk Properties of Great Plains Tar Oil Drum Samples and Average Properties Reported by ANG Coal Gasification Company

Property	REF 86-72A	REF 86-72B	Average Reported	REF 86-72AF ^a
Specific Gravity, 60/60°F	1.018	1.018	1.014	1.019
Water Content, wt %	1.5	1.4	2.0	1.7
ASTM D-2887 Distillation			TBP ^b	NDC
IBP, °F	200	198	225	
10%	354	351	354	
20%	396	395	399	
30%	423	420	435	
50%	513	510	525	
70%	617	611	637	
80%	686	681	711	
90%	774	771	804	
95%	834	831	NR ^d	
FBP	930	927	975	
ASTM D-86 Distillation		(Corr) ^e		ND
IBP, °F	275	320	210	
10%	379	388	250	
20%	409	413	360	
30%	443	440	400	
50%	544	502	440	
70%	587	601	520	
80%	607	660	640	
90%	--	737	690	
EP	643	824	NR	
Recovery, vol %	89	NR	NR	
Elemental Composition, as received ^e , wt %			NR	
Carbon	82.25	83.15		81.50
Hydrogen	8.60	8.70		8.70
Nitrogen	0.82	0.82		0.76
Sulfur	0.51	0.54		0.53
Oxygen (difference)	7.82	6.84		8.51
dry basis, wt %				
Carbon	83.50	84.33	87.70	82.91
Hydrogen	8.56	8.66	8.60	8.66
Nitrogen	0.83	0.83	0.60	0.77
Sulfur	0.52	0.55	0.40	0.54
Oxygen (difference)	6.59	5.63	2.70	7.12

^a REF 86-72AF is filtrate from REF 86-72A

^b True boiling point distillation

^c Not determined

^d Not reported

^e ASTM D-86 correlation derived from ASTM D-2887 distillation

Table 3. Component Analysis of Great Plains Tar Oil by Liquid-Liquid Extraction and Elution Chromatography

Fraction	Wt % of Oil	Wt % of Neutrals
Tar Bases (acid extract)	4.5	
Tar Acids (base extract)	19.8	
Neutrals (raffinate)	71.1	100
Loss	4.6	
Neutrals Subfractions (in order of elution)		
Saturates	6	8
Olefins/Alkylaromatics	23	33
Alkylaromatics	9	13
Aromatics	3	4
Alkylaromatic Carbonyls	4	6
Aromatic Carbonyls	3	4
Pyrrolics	3	4
Alkyl Hydroxyaromatics	5	7
Hydroxyaromatics	13	18
Loss	2	3

^a Includes water and solids

range from 7.7 to 9.8 wt %. However, tar acid component analyses also provided by ANG indicate that total contents of tar acid components (the total of phenol, cresols, ethylphenols, guaiacol and xylenols) in tar oil may range from a low of 5 wt % to a high of 16.2 wt %. These apparently conflicting data raise doubts about the actual range of tar acid content and the overall variability of tar oil composition.

Component analysis of neutral tar oil by elution chromatography (Table 3) shows it is mainly a mixture of aromatic hydrocarbons (~50 wt %), hydroxyaromatics (25 wt %), aromatic carbonyls (10 wt %), and saturates (8 wt %). Preliminary screening evaluation of neutral oil by combined gas chromatography/mass spectrometry (GC/MS) identified 186 components in more than 300 peaks that were clearly separated by gas chromatography. These identified components are estimated to represent about 90% of the neutral oil sample. Aromatic hydrocarbons are estimated to represent about 80% of the identified material. Naphthalene and the monomethylnaphthalenes are the most abundant aromatic hydrocarbons as a class. All hydrocarbon mass-spectral Z-series are represented from Z = -6 to Z = -26; Z = -32 was also observed. Alkyl-substituted homologs are observed for all the aromatic Z-series, and most alkyl substituents are methyl or ethyl. Saturated hydrocarbons in the form of n-alkanes were also identified with carbon numbers from 9 to 32. Alkenes were tentatively identified, and these were judged to be 1-alkenes based on retention times. Hydroxyaromatics were estimated at 10% of the neutral material. Phenols and cresols were not found in the neutral oil. Observation of the extensive series of n-alkanes in this oil, a by-

product of a high-temperature gasification process, is somewhat surprising because these compounds are relatively easy to crack.

Overall, component analyses indicate that 40-45 wt % of the tar oil is composed of oxygenated aromatic compounds, a fact which may ultimately be of considerable significance in the selection of process alternatives. Much of this oxygenated material is extractable tar acids, analogous to crude cresylic acids, a marketable commodity. Hydrogenation of tar oil to produce fuels without removing the tar acids will result in destruction of the cresylic acids, coupled with loss of a significant amount of hydrogen to water production. Extraction of tar acids before hydrogenation of the raffinate would reduce the amount of oil available for fuels production by some undetermined and perhaps highly variable amount.

Evaluation of analytical data on tar oils leads to the conclusion that tar oil composition is quite variable. The range of variability, particularly for tar acids content, could prove to be a key issue in the selection of the most profitable process alternatives. One process approach is suggested by a consideration of the boiling range of cresylic acid components.

The cresylic acid components boil from 359°F (182°C), the boiling point of phenol, to that of the highest boiling ethylphenols and xlenols (~437°F [225°C]). Thus a distillation range of about 350° to 450°F (177° to 232°C) should include all the cresylic acid components. Unfortunately, naphthalene also boils within this range (424°F [218°C]). Nevertheless, if a decision were made to remove cresylic acids, it could be practical to distill the tar oil to a cutpoint of about 450°F (232°C) to obtain a light distillate of about 35 vol % of the oil as a feedstock to extraction. Alkaline extraction of the distillate could yield a reasonably clean tar acid extract and a raffinate containing naphthalene and light aromatics to be recombined with the balance of the tar oil for fuels processing. This approach would reduce the size of an extraction unit to about a third the size needed to extract the whole tar oil, yield a cleaner extract, and reduce the oxygen content of the tar oil feed to hydrogenation. Caustic extraction of a tar-oil distillate and hydrogenation of a blend of the raffinate with tar oil heavy distillate are described in a later section of this report.

2. CRUDE PHENOLS ANALYSIS

Crude phenols extracted from plant process water are an important by-product with market potential as a source of chemicals. Bulk properties of the two drums of crude phenols, shipped from the plant, REF 86-73A and REF 86-73B, and typical average properties reported by ANG are listed in Table 4. Properties measured by WRI indicate that the two drums contain similar material. Specific gravity is somewhat lower and water contents somewhat higher than typical average values. ASTM D-2887 (simulated distillation by GC) data for WRI phenols drum samples and ASTM D-1160 distillation data for typical average phenols (ANG) indicate that the drum samples have a somewhat lower boiling range than the average over most of the range, but have about the same final boiling point within experimental error. Elemental composition data indicate

Table 4. Bulk Properties of Great Plains Crude Phenols Drum Samples and Average Properties Reported by ANG Coal Gasification Company

Property	REF 86-73A	REF 86-73B	Typical Ave. (ANG)
Specific Gravity, 60/60°F	1.066	1.066	1.072
Water Content, wt %	5.5	4.9	4.5
ASTM D-2887 Distillation			(ASTM D-1160)
IBP, °F	233	189	170
10%	341	340	265
20%	350	347	365
30%	358	355	380
50%	382	380	395
70%	401	399	465
80%	424	424	520
90%	476	476	560
95%	518	520	600
FBP, °F	766	722	765
ASTM D-86 Distillation		(Corr) ^a	
IBP, °F	222	311	210
10%	307	365	365
20%	376	366	380
30%	379	367	385
50%	391	375	395
70%	420	390	425
80%	471	392	470
90%	--	457	525
EP, °F	507	592 ^b	570
Recovery, vol %	92	NR	NR
Elemental Composition, wt %			
<u>as received</u>			
Carbon	71.30	71.80	NR
Hydrogen	7.40	7.20	
Nitrogen	0.47	0.53	
Sulfur	0.14	0.12	
Oxygen (difference)	20.69	20.35	
<u>dry basis</u>			
Carbon	75.45	75.18	79.00
Hydrogen	7.17	7.02	7.20
Nitrogen	0.50	0.55	0.40
Sulfur	0.15	0.13	0.20
Oxygen (difference)	16.73	17.12	13.20

^a ASTM D-86 correlation derived from ASTM D-2887 distillation

^b Not reported

the drum samples to be lower in carbon but higher in oxygen than average material. As was observed for the tar oils, the ASTM D-86 distillation data compare poorly in most respects. Properties of the WRI material appear to fall within the spread of the bulk property values reported by ANG.

Interpretation of mass spectra identified three major classes of compounds: monohydric phenols, dihydric/alkoxy phenols, and naphthols. Based on the fraction of total ionization for each class, monohydric phenols represent 77.1%, dihydric/alkoxy phenols represent 18.3%, and naphthols account for 2.2%. The remainder of total ionization is accounted for by light aromatic hydrocarbons, mostly toluene, xyliene, and naphthalene. The carbon number distribution for each of these classes is illustrated in Figure 1. Phenol (C-6) and the cresols (C-7) are dominant species in the monohydroxyaromatics. Dihydric phenols are predominantly methyl- or dimethyl-substituted. Overall, the monomethyl-substituted hydroxyaromatics are the most abundant components, followed closely by those with no alkyl substituents.

Arguments for isolating cresylic acids from crude phenols are much more compelling than for hydrogenating the phenols to produce fuel. ANG component analyses indicate that the average cresylic acids content is 63 wt % and can be as high as 82 wt %. The 350° to 450°F (177° to 232°C) boiling range for cresylic acid components represents about 65 vol % of the crude phenols, leaving only about 35 vol % for use as a supplementary feedstock for fuels production. If the crude phenols were hydroprocessed, it is calculated from reaction stoichiometry and phenols composition that about 25% of the hydrogen consumed would be lost to water production. The cresylic acids components would be converted mainly to low-boiling benzenes and cyclohexanes, at the expense of four moles of hydrogen per mole of phenol, cresol, or xlenol. Experiments reported in a later section demonstrate the extraordinarily high levels of hydrogen consumption when crude phenols are hydrogenated.

3. NAPHTHA ANALYSIS

Great Plains naphtha is a by-product extracted from the gas stream with cold methanol in a Rectisol extraction unit by a patented Lurgi process. The product is a highly volatile light naphtha material with a high sulfur content and an extremely noxious odor. Bulk properties and hydrocarbon composition data for raw naphtha, REF 86-74, are in Table 5, which show the naphtha is mostly composed of benzene and alkylbenzenes. The specific gravity of 0.821 compares favorably with the typical average plant value of 0.825. For boiling range comparison, only D-86 distillation data were provided by ANG, who report an initial boiling point (IBP) of 100°F (38°C) and an endpoint of 270°F (132°C). ASTM D-2887 distillation show an initial boiling point of 62°F (17°C) and a final boiling point of 364°F (184°C), with 95 vol % of the sample boiling at or below 276°F (136°C). Component analyses reported by ANG indicate that the raw naphtha is composed mostly of light aromatics and paraffins mixed with minor amounts of olefins, methanol, acetone, and methylethylketone. Much of the sulfur is incorporated in thiols, the primary source of the odor. Extraction of naphtha with aqueous 20% caustic solution reduced the sulfur content from 1.8 wt % to about

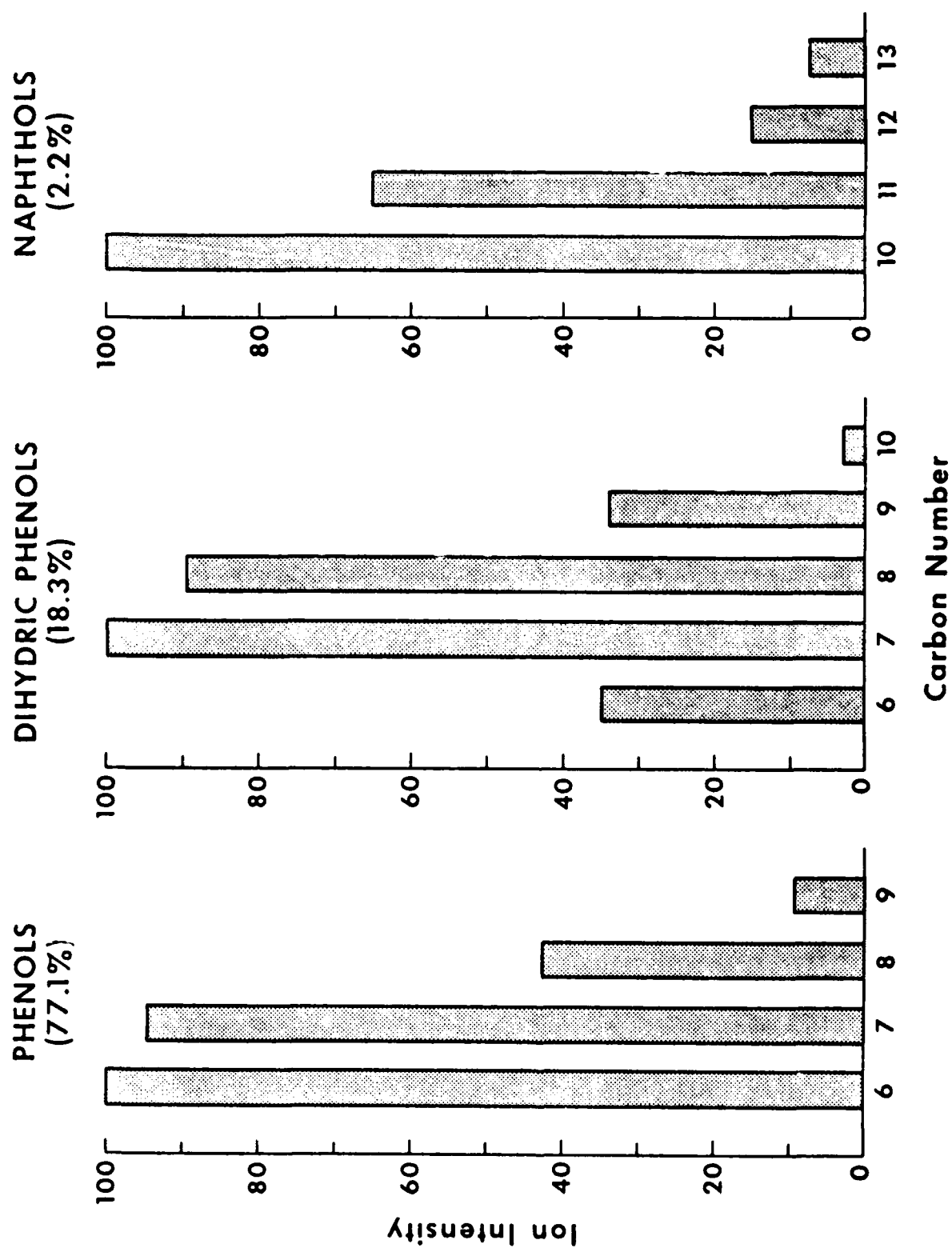


Figure 1. Carbon Number Distribution of Hydroxyaromatics in Crude Phenols

Table 5. Bulk Properties and Composition of Great Plains Naphtha, REF 86-74

Specific Gravity, 60/60°F	0.821
<u>Elemental Composition, wt % (ppm)</u>	
Carbon	85.0
Hydrogen	9.8
Nitrogen	0.18 (2071)
Sulfur	1.8 (18270)
Oxygen (difference)	3.2
<u>Distillation (ASTM D-2887)</u>	
IBP, °F	62
5/10	96/126
20/30	161/169
40/50	173/177
60/70	187/221
80/90	228/242
95	276
FBP, °F	364
<u>Benzene/Alkylbenzenes by GC/MS</u>	
<u>Carbon Number</u>	<u>% of Total Ionization</u>
6	73.6
7	14.7
8	2.5
9	0.6

0.6 wt % and markedly improved the odor, demonstrating a relatively simple desulfurization step and indirectly confirming the high thiols content. Assuming that two-thirds of the sulfur is present as ethanethiol, one-third is present as alkylthiophenes, and that nitrogen is represented by alkyipyridines, the composition of naphtha can be represented as 85-90 wt % monoaromatics (1-ring), 3-5 wt % sulfur compounds, about 1 wt % nitrogen compounds, and the balance oxygen compounds. These properties are sufficient to show that the naphtha is not suitable material for conversion to jet fuel, but could probably be converted to a light gasoline by mild hydrodesulfurization. Results of naphtha hydrogenation experiments are described in the last section.

SECTION III

HYDROGENATION SCREENING EXPERIMENTS

1. DESCRIPTION OF APPARATUS

The system used for hydrogenation of by-products is a typical bench-scale, fixed-bed system, operated in the downflow once-through mode. System pressure is controlled with dome pressure regulators, and hydrogen flow is regulated by a mass flow controller. Liquid feed is regulated by a Hruska precision pump. The reactor temperature is controlled by a four-section clamshell-type tube furnace, each section regulated to within $\pm 0.5^{\circ}\text{F}$ by an electronic proportioning controller. The liquid product is collected in a stainless steel receiver at room temperature at 250 psig. Gases leaving the receiver are analyzed on-line by temperature-programmed gas chromatography. The reactors used for these experiments are stainless steel cylinders, either 41 1/2-inch x 1-inch o.d. x 3/3-inch i.d., or 41 1/2-inch x 1-inch o.d. x 9/16-inch i.d. The system is manually controlled with computerized monitoring and data acquisition.

2. PREPARATION OF CATALYST AND OPERATING PROCEDURE

All experiments were conducted with Shell 424 catalyst provided in the form of a 1/10-inch-diameter tri-lobe extrudate. This is a widely used, commercially available Ni-Mo type in which the metals are supported on silica-improved alumina acidified with phosphoric acid. It was selected for its saturation and cracking capabilities, and for its resistance to deactivation by nitrogen or sulfur.

The catalyst bed was prepared in three sections of equal volume with 1-inch layers of Berkshire sand at the top and bottom and between the sections. Sand was also dispersed in each section to partially fill the spaces between catalyst particles. Each section was supported by stainless steel screen at the top and bottom. This packing plan was intended to minimize channelling and to dilute the catalyst. It provided a catalyst bed that filled that portion of the reactor enclosed by the furnace heating elements. The 5 5/8-inch section of the reactor above the catalyst bed was filled with coarse inert alumina particles, serving as a preheat section.

The catalyst was presulfided with 5% H_2S in hydrogen according to the Shell procedure, modified to compensate for Laramie's barometric pressure (nominally 585 torr). At a system pressure of 5 psig (instead of 1 atm.), $\text{H}_2\text{S}/\text{H}_2$ flow was established at 60 L/hr (10 L/hr per each 10 cc catalyst) at room temperature. The reactor temperature was raised to 400°F (204°C) and held at that temperature for two hours, then raised to 600°F (316°C) and held there for one hour, and then raised to 700°F (371°C) and held there for two hours. The $\text{H}_2\text{S}/\text{H}_2$ flow was then reduced to ~ 5 L/hr while the reactor temperature was reduced to $\sim 250^{\circ}\text{F}$ (121°C). Pure hydrogen and liquid feed were then introduced at the top of the reactor, while the temperature was brought to the preselected starting value.

In a normal one- to two-week operation, the reactor temperature was stabilized at the first selected experimental temperature and the product oil gravity and hydrogen content were monitored at intervals for 48 hours. All product collected during this period was rejected. Thereafter, a sample representing about seven hours of production was collected for analysis, and the reactor temperature was adjusted to the next experimental temperature. The next 16-17 hours of production were rejected, and a sample of process liquid representing 6-8 hours production was collected for analysis. This cycle was repeated after each change of conditions for the run duration.

Process intermediates were prepared for analysis as follows. The liquid was transferred from the receiver to a separatory funnel, weighed, and washed with cold water to remove hydrogen sulfide and ammonia. The organic phase was dried by stirring overnight with anhydrous barium sulfate in a closed container. The mixture was filtered to remove the salt and samples of the filtrate were submitted for analysis. Excess filtrate was stored under nitrogen in sealed, refrigerated glass containers.

3. HYDROGENATION OF CRUDE TAR OIL

All experiments were conducted at 2,000 psig in the temperature range of 650°F (343°C) to 750°F (399°C) and at liquid hourly space velocities (LHSV) of 1.0, 0.5, or 0.33 volumes liquid feed per volume catalyst per hour. Hydrogen feed ratios were 6,000, 10,750, or 16,000 standard cubic feet per barrel (scfb) liquid feed.

Two series of 1-week hydrogenation experiments were completed on whole crude tar oil REF 86-72A, producing six process intermediates. In the first series, products were collected at 650°, 675°, and 700°F (343°, 357°, and 371°C). In the second series, products were collected at 700°, 725°, and 750°F (371°, 385°, and 399°C). Both series were conducted at LHSV = 1.0 and a hydrogen feed ratio of 6,000 scfb. Hydrogen consumption for the first series ranged from 2,600 scfb at 650°F (343°C) to 3,000 scfb at 700°F (371°C). For the second series, hydrogen consumption values were 3,127 scfb at 700°F (371°C), 2935 scfb at 725°F (385°C), and 2,895 scfb at 750°F (399°C). The trend in hydrogen consumption was thus in the expected direction from 650°F (343°C) to 700°F (371°C), but reversed from 700°F (371°C) to 750°F (399°C). This trend reversal may have been caused by operating before catalyst line-out (nonsteady-state operation), by insufficient hydrogen feed, by nonuniform flow, or all three. Both runs were plagued by intermittent flow problems that were apparently caused by particulate matter in the oil.

About three days into the first series, the outlet pressure of the liquid feed pump began to increase, and at the end of 4 1/2 days, the pressure had increased from the original 2,100 psig to over 4,000 psig, at which time the run was terminated. The metal in-line filter was disassembled, and the filter element was found to contain about 15 grams of black goo. Extraction of this material with methylene chloride left 4-5 g of fine particles. This residue was a mixture of tan particles, probably coal ash or dirt, and black carbon or coal particles.

Because high-temperature hydrogenolysis of oxygen compounds produces steam that might attack the crystalline structure of the catalyst, the reactor was unpacked to see if there was evidence of catalyst breakdown. However, the catalyst particles were apparently intact.

The second series of hydrogenation experiments was conducted without an in-line filter, with flow problems again developing about 3 days into the run. It became more and more difficult to maintain hydrogen flow, and the run was terminated at 4 1/2 days, after collecting three more products. After catalyst burn-off at 700°F (371°C) in a stream of air, the reactor was unpacked by sections. Fine particulates were found in the top section, and after screening out coarse inerts and catalyst, this material was submitted for metals analysis by inductively coupled argon plasma (ICAP) scan. Five gallons of oil were filtered through a Balston cartridge and a sample of the tarry filter residue was also submitted for metals analysis. Results of these analyses are found in Table 6. The metals suite is typical for metals found in sections across a North Dakota lignite formation (reference 3). The particulate matter in the tar oil is thus assumed to be entrained coal ash and clay mineral from mine-run lignite.

**Table 6. Metals Found in Great Plains Tar Oil Solids by ICAP Scan
(Metals Content in mg/kg)**

Metal	Filter Resid. 86-03-4	Reactor Fines 86-03-5
Aluminum	1,800	40,500
Arsenic	<21	1,390
Boron	38.2	112
Barium	640	12,500
Calcium	8,200	86,400
Bismuth	67.3	1,330
Cadmium	75.0	1,490
Cobalt	<2.1	56.5
Chromium	8.9	383
Copper	29.1	824
Sodium	1,720	16,200
Iron	2,860	125,000
Potassium	<1,040	2,260
Lithium	<2.1	64.2
Magnesium	1,850	26,800
Manganese	52.5	506
Molybdenum	<4.2	595
Nickel	11	2,200
Phosphorus	<208	1,750
Lead	206	3,920
Selenium	<21	568
Silicon	32,200	180,000
Strontium	314	4,790
Zinc	87.4	992

A third hydrogenation series was conducted with the in-line filter in place, using filtered tar oil, REF 86-72AF. Erratic flow problems were not observed until well into the fourth day of operation, and were less severe than in the previous runs. Hydrogen consumption values were not substantially different than those observed in the previous series. However, hydrogen consumption did increase with increased temperature in contrast to the trend observed in the preceding experiment. Fine particulate matter was again found in the top section of the catalyst bed, indicating that particles small enough to pass through the in-line 10-micron filter element remained in the oil, and could eventually cause plugging problems in fixed-bed hydrogenation.

Results of these first three series of experiments, including hydrogenation conditions, average hydrogen consumption values, and product properties are summarized in Tables 7, 8, and 9. Comparison of product properties with reaction conditions reveals only one fairly consistent trend, which is the decline in density with increasing reactor temperature. This trend is supported by distillation data that show that the product boiling range broadened and lowered with increasing reaction temperature. Neither the hydrogen content of the product nor the degree of aromatics saturation change with temperature in a consistent manner. Five of these first six products contain residual oxygen compounds, and all six products contain more than 28 wt % aromatics. The results indicate that more than 3,100 scfb hydrogen must be consumed to eliminate oxygen and to reduce aromatics content to acceptable levels.

Table 8 includes calculated average composition values based on GC/MS analysis for the 175-600°F (79-316°C) distillate from the three products obtained in the second hydrogenation series. The values demonstrate that the average composition of this distillate, which includes virtually the entire boiling range of JP-4 and JP-8 jet fuels, would contain over 35 wt % aromatics plus residual hydroxyaromatics. Products from the first series (Table 7) would predictably yield a distillate containing over 40 wt % aromatics. Based on comparisons of values for hydrogen contents and density, the average distillate from the third set of products (Table 9) would have about the same composition as shown for the hypothetical distillate represented in Table 8. In sum, the data show that these products were not sufficiently saturated to serve as sources for jet fuel.

Failure of these experiments to yield sufficiently hydrogenated products is attributed partly to insufficient hydrogen supply, further complicated by system upsets caused by particulates plugging. Although these products may not represent those from optimal or steady-state conditions, useful insights were gained from these experiments.

It was apparent that particulate matter would have to be removed from the tar oil before it could be successfully hydrogenated in our fixed-bed system. Comparison of product properties with crude tar oil properties indicated that the highest boiling 10% of the oil was little affected and probably very resistant to hydrogenation, which is to be expected for multi-ring condensed aromatic systems. It was also apparent that consumption of hydrogen equivalent to 3,100 scfb was insufficient to reduce total aromatics content to the range of interest.

Table 7. Process Conditions and Properties of Three Hydrogenated Products from Great Plains Tar Oil REF 86-72A

	Product Number		
	86-01-1	86-01-2	86-01-3
<u>Process Conditions</u>			
Pressure, psig	2,000	2,000	2,000
Temperature, °F	650	675	700
LHSV	1.0	1.0	1.0
H ₂ Feed Rate, scfb	6,000	6,000	6,000
H ₂ Consumption, scfb	2,606	2,828	3,000
<u>Product Properties</u>			
Specific Gravity, 60/60°F	0.883	0.872	0.867
Elemental Composition, wt % (ppm)			
Carbon	87.5	87.0	86.8
Hydrogen	12.5	12.9	13.2
Nitrogen	(280)	(50)	(15)
Sulfur	(<20)	(<20)	(<20)
Oxygen	0	~0.1	0
Distillation (ASTM D-2887)			
IBP	159	144	147
5/10	214/250	201/226	200/225
20/30	314/371	291/343	288/346
40/50	409/453	394/438	391/430
60/70	501/553	484/532	476/522
80/90	620/719	599/696	586/681
95	792	774	761
FBP	923	899	885
Compound Class by GC/MS, wt %			
Paraffins	18.0	27.3	21.1
Monocycloalkanes	28.4	32.7	29.9
Dicycloalkanes	4.5	7.2	8.7
Total Saturates	50.9	67.2	59.7
Alkylbenzenes	16.4	10.6	12.1
Indanes/Tetralins	25.7	19.6	21.5
Dihydronaphthalenes	1.5	0.0	4.6
Dihydrofluorenes	2.0	1.2	0.9
Fluorenes	1.7	0.4	1.2
Phenanthrenes/Anthracenes	1.4	ND ^a	ND
Total Aromatics	48.7	31.8	40.3
Naphthols	0.4	1.0	ND

^a Not detected

Table 8. Process Conditions and Properties of Three Hydrogenated Products from Great Plains Tar Oil and Calculated Properties of Average 175-600°F Distillate

Product Number	Product Number			Calc. Average (175-600°F) ^a
	86-02-1	86-02-2	86-02-3	
<u>Process Conditions</u>				
Pressure, psig	2,000	2,000	2,000	
Temperature, °F	700	725	750	
LHSV	1.0	1.0	1.0	
H ₂ Feed Rate, scfb	6,000	6,000	6,000	
H ₂ Consumption, scfb	3,127	2,935	2,895	
<u>Product Properties</u>				
Specific Gravity, 60/60°F	0.870	0.865	0.861	
Elemental Composition, wt % (ppm)				
Carbon	87.1	87.2	86.7	
Hydrogen	12.8	12.5	12.7	
Nitrogen	(<20)	(<10)	(<10)	
Sulfur	(<20)	(<20)	(<20)	
Oxygen (difference)	~ 0.1	~0.2	~0.5	
Distillation (ASTM D-2887), °F				
IBP	155	136	135	175
5/10	209/227	205/222	193/218	
20/30	289/346	284/341	277/334	
40/50	395/435	391/428	383/418	
60/70	480/525	472/518	461/505	
80/90	589/683	581/675	568/658	
95	762	752	738	
FBP	885	883	867	600
Compound Class by GC/MS, wt %				
Paraffins	29.9	29.7	24.6	17.1
Monocycloalkanes	32.5	26.6	34.1	31.9
Dicycloalkanes	5.4	5.3	7.2	8.0
Total Saturates	67.8	61.6	65.9	57.0
Alkylbenzenes	5.7	8.3	8.3	7.9
Indanes/Tetralins	18.7	21.4	15.3	24.7
Naphthalenes	3.4	1.3	2.8	3.0
Dihydrofluorenes	0.7	1.1	0.9	1.0
Fluorenes	0.6	0.8	0.2	0.3
Phenanthrenes/ Anthracenes	0.3	0.4	0.4	0.3
Dihdropyrenes	0.1	0.3	0.0	0.2
Fluoranthenes	0.0	0.2	0.3	0.0
Total Aromatics	29.5	33.6	28.2	37.4

Table 8. Continued

Product Number	Product Number			Calc. Average (175-600°F) ^a
	86-02-1	86-02-2	86-02-3	
Phenols	ND ^b	0.7	ND	0.2
Naphthols	2.7	4.1	5.9	5.4
Wt % of Product	100	100	100	75.2

^a Calculated composition of a blend of 175-600°F true boiling point distillates prepared by blending equal volumes of distillate from 86-02-1, 86-02-2, and 86-02-3.

^b Not detected

Calculated minimum hydrogen requirements to remove all heteroatoms and to reduce aromatics concentration to 30 wt % is about 2,700 scfb, assuming that only heteroatom-containing rings are opened and no other ring opening or carbon-carbon bond cleavage occurs. However, the high paraffin content of the products (25-30 wt %) gives evidence that other rings were opened to yield acyclic saturated products, which further increased hydrogen consumption. Because neither these extra hydrogen-consuming reactions nor the hydrogen lost in solution in liquid products is assumed in the calculation, the consumption values shown in the tables, which range from 2,800 to 3,100 scfb, are well within reason.

From the insights gained in these first experiments, we concluded that all further tar oil experiments should be conducted with distilled feedstocks. The distillation procedure and subsequent experiments are described in following sections.

4. TAR OIL DISTILLATION, EXTRACTION, AND BLENDING

The crude oil was distilled in two passes through an Artisan turbo-molecular still, a continuous-feed flash distillation unit. In the first pass, a light distillate boiling in the nominal IBP-450°F (IBP-232°C) range was collected at ambient (585 torr) pressure. Residual oil was then fed to a second pass at 10 torr to collect a heavy distillate boiling in the nominal 450-750°F (232-399°C) range. The light distillate was extracted 3 times with half its volume of aqueous 30% sodium hydroxide solution, and the raffinate oil was water-washed to remove residual caustic. A portion of the raffinate oil was mixed with twice its volume of heavy distillate to form a partially upgraded feedstock blend.

Distillation of 93.4 liters of tar oil yielded 25 liters (25 wt %) of light distillate and 51.5 liters (56 wt %) of heavy distillate. The residue was 16 wt % of the charge, and 3 wt % was lost to evaporation and handling. Caustic extraction of light distillate yielded about 17 liters of raffinate oil. Characteristics of the crude tar oil, the

**Table 9. Process Conditions and Properties of Hydrogenation
Products from Filtered Great Plains Tar Oil
REF 86-72AF on Shell 424 Ni-Mo Catalyst**

Product Number	Product Number		
	86-03-1	86-03-2	86-03-3
<u>Process Conditions</u>			
Pressure, psig	2,000	2,000	2,000
Temperature, °F	700	725	750
LHSV, V_0/V_c /hr	1.0	1.0	1.0
H ₂ Feed Rate, scfb	6,000	6,000	6,000
H ₂ Consumption, scfb	2,802	2,842	2,958
<u>Product Properties</u>			
Specific Gravity, 60/60°F	0.868	0.862	0.860
Elemental Composition, wt % (ppm)			
Carbon	87.4	87.3	86.7
Hydrogen	12.6	12.7	13.2
Nitrogen	(18)	(<10)	(<10)
Sulfur	(<20)	(<20)	(<20)
Oxygen (difference)	0	0	0
Distillation (ASTM D-2887), °F			
IBP	149	137	140
5%	204	200	200
10%	229	218	219
20%	295	284	283
30%	355	344	342
50%	446	431	425
70%	535	521	513
80%	598	584	575
90%	688	678	663
95%	767	758	742
FBP	895	890	880

distillates, and the raffinate-heavy distillate blend are listed for comparison in Table 10. The low efficiency of the distillation is reflected by the boiling range overlap in the distillates, which shows that each distillate included 15-20 vol % of material boiling above the intended maximum temperature. However, the main objectives of the distillation were achieved, which were to concentrate lower-boiling oxygen compounds in the light distillate and to reject particulate matter in the residue. Caustic extraction of cresylic acid components from the light distillate was much easier than attempting to extract them from the whole crude tar oil, which generally resulted in formation of a stable emulsion.

Table 10. Characteristics of Tar Oil, Flash Distillates, and Raffinate-Distillate Blend

	REF 86-72A Tar Oil	87-08-3 IBP-450°F	87-08-4 450-750°F	87-08-9 Blend ^a
Specific Gravity, 60/60°F	1.018	0.953	1.028	0.982
Carbon	83.5	80.6	81.7	84.2
Hydrogen	8.6	9.2	8.3	9.0
Nitrogen	0.8	0.6	0.7	0.7
Sulfur	0.5	0.5	0.6	0.6
Oxygen (difference)	6.6	9.1	8.7	5.5
Distillation (ASTM D-2887)				
IBP, °F	200	171	278	223
5/10	318/354	235/284	368/397	294/342
20/30	396/423	337/364	438/483	395/422
40/50	469/513	384/401	522/577	459/497
60/70	559/617	412/432	597/644	534/583
80/90	686/774	458/506	695/762	647/731
95	834	543	813	791
FBP, °F	930	674	908	908
Vol % of Tar Oil	100	27	55	73

^a Blend of one volume raffinate from caustic extraction of 87-08-3 with two volumes of heavy distillate 87-08-4.

The heavy distillate and the raffinate-distillate blend were feedstocks for further hydrogenation experiments described in the succeeding subsections.

5. HYDROGENATION OF HEAVY DISTILLATE 87-08-4

Hydrogenation was conducted at 2,000 psig, a hydrogen feed ratio of 6,000 scfb, and 575-675°F (302-357°C) at LHSV = 0.5 or 650-700°F (316-371°C) at LHSV = 1.0. Eight products were collected in 245 hours of continuous operation during which no flow problems developed. However, analytical results showed the heavy distillate to be even more resistant to deoxygenation and saturation than the whole tar oil. None of the products were suitable as a source for jet fuel. At LHSV = 1.0, oxygen was found in all but the 700°F (371°C) product. At LHSV = 0.5, products generated at temperatures of 650°F (343°C) or lower contained oxygen at concentrations of 0.8 wt % or more and more than 700 ppm nitrogen. All these marginal products were unstable after exposure to air and room light, shown by color changes during the drying process. Properties of the eight products and hydrocarbon compositions of the two best products are found in Table 11. The two best products represent similarly high

**Table 11. Process Conditions and Properties of Hydrogenation Products
from Tar Oil Heavy Distillate 87-08-4**

	Product Number			
	123-93-87-09-2	123-93-87-09-1	123-93-87-09-3	123-93-87-09-8
<u>Process Conditions</u>				
Pressure, psig	2,000	2,000	2,000	2,000
Liquid hourly space velocity	1.0	1.0	1.0	1.0
Temperature, °F	650	675	700	650
Hydrogen feed, scfb	6,000	6,000	6,000	6,000
Time on stream, hr	42	36	80	200
Hydrogen Consumption, scfb	2,602	2,918	3,032	2,545
<u>Product Characteristics</u>				
Specific gravity, 60/60°F	0.887	0.872	0.865	0.887
Elemental composition, wt % (ppm)				
Carbon	87.1	87.3	87.4	87.2
Hydrogen	12.0	12.5	12.7	12.0
Nitrogen	(293)	<25	<25	(338)
Sulfur	<35	<34	<35	<35
Oxygen (difference)	0.9	0.2	0	0.8
Distillation (ASTM D-2887)				
IBP/5	162/218	152/209	133/210	163/217
10/20	271/355	254/334	249/329	270/354
30/40	405/452	391/432	385/423	404/450
50/60	490/526	472/506	462/499	488/526
70/80	572/620	549/600	535/587	572/621
90/95	699/766	677/752	663/740	700/767
FBP	877	866	864	875
<u>Hydrocarbon Class, wt %</u>				
Paraffins			7.7	
Monocycloalkanes			10.7	
Dicycloalkanes			8.8	
Tricycloalkanes			1.2	
Total Saturates			28.4	
Alkylbenzenes			13.5	
Indanes/Tetralins			56.2	
Naphthalenes			1.3	
Fluorenes			0.5	
Anthracenes/Phenanthrenes			0.1	
Total Aromatics			71.6	

Table 11. Continued

	Product Number			
	123-93-87-09-2	123-93-87-09-1	123-93-87-09-3	123-93-87-09-8
<u>Process Conditions</u>				
Pressure, psig	2,000	2,000	2,000	2,000
Liquid hourly space velocity	0.5	0.5	0.5	0.5
Temperature, °F	575	600	625	675
Hydrogen feed, scfb	6,000	6,000	6,000	6,000
Time on Stream, hr	176	152	104	245
Hydrogen Consumption, scfb	1,564	1,967	2,372	3,131
<u>Product Characteristics</u>				
Specific gravity, 60/60°F	0.942	0.918	0.872	0.865
Elemental composition, wt % (ppm)				
Carbon	86.6	86.3	87.3	87.2
Hydrogen	10.6	11.1	11.8	12.9
Nitrogen	(4830)	(2680)	(769)	<35
Sulfur	(159)	(57)	<35	<25
Oxygen (difference)	2.3	2.3	0.8	0
Distillation (ASTM D-2887)				
IBP/5	173/275	173/251	166/236	164/213
10/20	351/406	314/396	290/375	264/346
30/40	449/488	439/480	420/465	392/436
50/60	526/565	517/555	505/541	472/504
70/80	608/660	598/652	585/637	541/592
90/95	735/790	729/786	719/779	670/747
FBP	894	894	891	866
<u>Hydrocarbon Class, wt %</u>				
Paraffins				8.8
Monocycloalkanes				14.2
Dicycloalkanes				12.9
Tricycloalkanes				2.5
Total Saturates				38.4
Alkylbenzenes				10.3
Indanes/Tetralins				50.6
Naphthalenes				0.6
Fluorenes				0.1
Anthracenes/Phenanthrenes				0.0
Total Aromatics				61.6

levels of hydrogen consumption and have the same density. The differences in composition, although not large, indicate an advantage in conversion at the lower space velocity. The product generated at LHSV = 0.5 and 675°F (357°C) has higher hydrogen content, higher content of material boiling in the 200-600°F (93-316°C) (jet fuel) range, and 10 wt % lower aromatics content. Based on these criteria, the product of lower space velocity and lower temperature is the better product. Unfortunately, neither product is sufficiently saturated for jet fuel, and these experiments again left some doubt that the hydrogen supply was adequate to reach optimal saturation. There was also doubt that reactor temperatures were high enough. These questions were addressed by substantially increasing the hydrogen feed ratio and extending the temperature range to 750°F (399°C) in the next hydrogenation series, conducted with the blended distillate.

6. HYDROGENATION OF RAFFINATE-DISTILLATE BLEND 87-08-9

The catalyst volume was increased to 120 cc for this experimental series to permit collection of larger quantities of products at lower space velocities over a limited run period. Five products were collected in a continuous 2-week run at two sets of conditions. For one experiment, conditions were 2,000 psig, LHSV = 0.5, hydrogen feed ratio was 10,750 scfb, with products collected at 675°, 700°, and 720°F (357°, 371, and 382°C). For the other experiment, conditions were 2,000 psig, LHSV = 0.33, hydrogen feed ratio 16,000 scfb with products collected at 700°F (371°C) and 750°F (399°C). These conditions were intended to provide a large excess of hydrogen to insure the maximum saturation at these conditions while exploring the temperature limit for achieving adequate saturation. Hydrogenation conditions, hydrogen consumption values, and product characteristics of the four best products are listed in Table 12. These products are completely deoxygenated, nitrogen and sulfur contents are below 30 ppm, and residual naphthalenes and heavier aromatics are at trace levels. Their high levels of dicycloalkanes and indanes or tetralins offer good prospects for grade JP-8 jet fuel of higher than average density, although the paraffins content is considerably higher than the 10% maximum specified for JP-8X. Calculated compositions of various fuel distillates available from each product showed that a blend of intermediate products could yield a distillate that might meet specifications for either a conventional JP-8 or a JP-8X. Since preparation of both these fuel grades was among the objectives of this investigation, test fuel distillates representing both grades were prepared. Preparation and characteristics of the test fuels are described in Section IV.

7. HYDROGENATION OF CRUDE PHENOLS

Hydrogenation was conducted at 2,000 psig system pressure on a 60-cc bed of presulfided Shell 424 catalyst prepared as previously described. A series of products was obtained at liquid hourly space velocities of 0.5 and 1.0 and at temperatures from 550°F (289°C) to 650°F (343°C). The hydrogen feed rate was equivalent to 6000 standard cubic feed per barrel liquid feed. The objectives were to identify the least severe conditions at which hydroxyaromatics were eliminated and to measure the distribution of compound classes in the fully deoxygenated products.

Table 12. Process Conditions and Properties of Hydrogenation
Products from Tar Oil Raffinate-Heavy Distillate
Blend 87-08-9

	Product Number	
	367-8-87-11-3	367-8-87-11-5
<u>Process Conditions</u>		
Pressure, psig	2,000	2,000
Reactor Temperature, °F	700	720
LHSV, V_0/V_C /hr	0.5	0.5
H ₂ Feed Ratio, scfb	10,750	10,750
H ₂ Consumption, scfb	3,250	3,468
<u>Product Characteristics</u>		
Specific Gravity, 60/60°F	0.837	0.834
Hydrogen, wt %	13.4	13.5
Paraffins, wt %	20.8	23.1
Monocycloalkanes	17.4	17.1
Dicycloalkanes	29.0	27.6
Tricycloalkanes	2.0	2.0
Total Saturates	69.2	69.8
Alkylbenzenes	18.0	17.1
Indanes/Tetralins	12.7	13.1
Naphthalenes	0.1	trace
Total Aromatics	30.8	30.2
<u>Distillation (ASTM D-2887)</u>		
IBP, °F	141	130
5/10	209/240	207/238
20/30	299/347	296/346
40/50	373/400	372/399
60/70	439/478	436/475
80/90	523/603	521/601
95	683	680
FBP	844	843

Table 12. Continued

	Product Number	
	367-8-87-11-6	367-8-87-11-7
<u>Process Conditions</u>		
Pressure, psig	2,000	2,000
Reactor Temperature, °F	700	750
LHSV, V_o/V_c /hr	0.33	0.33
H ₂ Feed Ratio, scfb	16,000	16,000
H ₂ Consumption, scfb	3,533	3,780
<u>Product Characteristics</u>		
Specific Gravity, 60/60°F	0.839	0.829
Hydrogen, wt %	13.4	13.7
Paraffins, wt %	21.8	21.6
Monocycloalkanes	17.0	27.5
Dicycloalkanes	28.3	30.5
Tricycloalkanes	2.4	1.9
Total Saturates	69.5	81.5
Alkylbenzenes	17.8	9.3
Indanes/Tetralins	12.7	8.8
Naphthalenes	0	0.1
Fluorenes	0	0.0
Total Aromatics	30.5	18.5
<u>Distillation (ASTM D-2887)</u>		
IBP, °F	153	131
5/10	211/248	205/233
20/30	307/351	287/337
40/50	377/406	364/391
60/70	445/484	422/462
80/90	530/611	508/581
95	693	657
FBP	847	827

Characteristics of water-free product liquids generated at space velocities 1.0 and 0.5 are presented in Table 13. The data indicate that at either space velocity, oxygen compounds are residual in products collected at temperatures of 575°F (302°C) or lower. As expected, the impact on composition was significantly greater at LHSV 0.5, illustrated by comparing hydrogen contents and specific gravities of products generated at 575°F (302°C) and 600°F (316°C) at each space velocity. From the fuels production viewpoint, little useful change in composition was realized at process temperatures above 600°F (316°C).

Table 13. Characteristics of Products of Hydrogenation of Crude Phenols on Shell 424 Ni-Mo Catalyst--Process Conditions and Product Properties

	Product Number			
	87-07-2	87-06-1	87-07-8	87-06-3
<u>Process Conditions</u>				
Pressure, psig	2,000	2,000	2,000	2,000
Temperature, °F	575	600	625	650
LHSV	1.0	1.0	1.0	1.0
H ₂ Feed Rate, scfb	6,000	6,000	6,000	6,000
H ₂ Consumption, scfb	2,790	4,411	4,335	4,352
<u>Product Properties</u>				
Specific Gravity, 60/60°F	0.881	0.803	0.797	0.800
Elemental Composition, wt % (ppm)				
Carbon	84.6	86.2	85.7	86.7
Hydrogen	12.1	13.8	13.9	13.8
Nitrogen	0.2	(<25)	(<25)	(<25)
Sulfur	(88)	(120)	(35)	(25)
Oxygen	3.1	--	--	--
Distillation (ASTM D-2887)				
IBP, °F	153	135	129	135
5%	169	165	164	165
10%	177	169	170	170
20%	198	179	179	179
30%	214	188	190	187
50%	300	216	216	216
70%	358	257	254	245
80%	377	287	279	274
90%	416	404	368	359
95%	510	490	449	445
FBP, °F	752	771	642	667
Hydrocarbon Class, wt %				
Paraffins	9.3	11.0	14.5	11.2
Monocycloalkanes	83.6	80.6	79.8	80.9
Dicycloalkanes	Trace	0.2	0.2	0.2
Tricycloalkanes ^a	2.5	0	0	0
Total Saturates	95.4	91.8	94.5	92.3
Alkylbenzenes	3.1	5.4	4.9	6.7
Indanes/Tetralins	1.2	2.8	0.6	1.0
Naphthalenes	0.1	0	0	0
Fluorenes	Trace	0.1	Trace	0
Total Aromatics	4.4	8.3	5.5	7.7

Table 13. Continued

	Product Number		
	87-07-3	87-07-4	87-07-5
<u>Process Conditions</u>			
Pressure, psig	2,000	2,000	2,000
Temperature, °F	550	575	600
LHSV	0.5	0.5	0.5
H ₂ Feed Rate, scfb	6,000	6,000	6,000
H ₂ Consumption, scfb	2,270	4,317	4,983
<u>Product Properties</u>			
Specific Gravity, 60/60°F	0.934	0.810	0.793
Elemental Composition, wt % (ppm)			
Carbon	80.3	85.0	85.7
Hydrogen	11.0	13.9	14.2
Nitrogen	0.4	(309)	(<25)
Sulfur	(128)	(37)	(<37)
Oxygen	8.3	1.0	--
Distillation (ASTM D-2887)			
IBP	159	148	138
5%	176	174	165
10%	185	178	172
20%	216	185	180
30%	281	204	195
50%	344	221	216
70%	375	271	259
80%	393	341	289
90%	450	414	397
95%	554	492	472
FBP	826	735	704
Hydrocarbon Class, wt %			
Alkanes	2.2	12.1	13.4
Monocycloalkanes	79.6	85.7	84.8
Dicycloalkanes	0	0.1	0.1
Tricycloalkanes ^a	7.5	0.3	0
Total Saturates	89.3	98.2	98.3
Alkylbenzenes	7.8	1.33	1.5
Indanes/Tetralins	2.5	0.5	0.2
Naphthalenes	0.2	0	0
Fluorenes	0	0	0
Total Aromatics	10.5	1.8	1.7

^a Includes phenols

The presence of residual hydroxyaromatics in products is manifested indirectly by GC/MS hydrocarbon composition data. Products generated at 550°F (288°C) and 575°F (302°C) are shown to contain measurable amounts of tricycloalkanes not found in products collected at 600°F (316°C) or at higher temperature. However, phenols were easily detected in the 550°F (288°C) and 575°F (302°C) products by odor, and their presence was confirmed by infrared spectrometry. However, the residual phenols were interpreted by the mass-spectral computer program as hydrocarbons grouped in the -4 mass-spectral Z-series where tricycloalkanes normally are found. The values shown for tricycloalkanes are thus artifacts of a computer program applicable only to hydrocarbon mixtures and serve only to indicate the presence of phenols.

The major hydrocarbon class found in the fully deoxygenated products was monocyclic alkanes, represented by cyclohexane and methylcyclohexane. Cyclohexane was the major component, and no cycloalkane with more than eight carbon atoms was detected. In the product obtained at 600°F (316°C) and 1.0 space velocity, cyclohexanes, as a class, represented 80 wt % of the total hydrocarbon, and the ratio of cyclohexane to methylcyclohexane was greater than two. This observation is evidence of dealkylation or ring opening, since simple hydrogenation would lead to methylcyclohexane as the predominant product, on the basis of the predominance of methyl-substituted hydroxyaromatics in the feedstock. Further evidence is provided by the carbon number distribution observed for benzenes, the major class of aromatics found in the products and the logical precursors to the cyclohexanes. Carbon numbers for the product benzenes ranged from 6 to 9, found in the order $C_7 > C_8 > C_6 > C_9$. The expected order by simple deoxygenation would be $C_7 > C_6 > C_8 > C_9$, and further saturation would be expected to preserve this order in the cyclohexanes. Because cyclohexane is the major saturation product and no C_8 or C_9 cyclohexanes are found in products, we conclude that dealkylation and ring opening occur during or after deoxygenation. Ring opening is also demonstrated by the increase in paraffin concentration observed in products as reaction temperature is increased. About 90 vol % of the fully deoxygenated products boils in the JP-4 distillate range, and about 40 vol % boils in the JP-8 range. However, the high consumption of hydrogen to produce water and low-boiling products in low yields does not favor the use of crude phenols for fuels production.

8. HYDROGENATION OF NAPHTHA

A series of naphtha hydrotreating experiments were performed under the following conditions: catalyst, Shell 424 Ni-Mo; catalyst volume, 60 cc; LHSV 1.0; pressure, 500 psig; hydrogen feed ratio, 1,500 standard cubic feed per barrel; reactor temperatures 300-500°F (149-260°C). Hydrogen consumption values and bulk characteristics of three products are found in Table 14, which also lists the quantities of the two hydrocarbon types found in the best product. These intermediate products are essentially light gasoline. Unfortunately, the process severity required to reduce the nitrogen and sulfur content to acceptable levels also saturated more than half the naphtha benzenes and resulted in a higher than desirable hydrogen consumption. This trend toward aromatics saturation might be reversible by employing higher reaction temperatures. It would be advantageous to retain the highest

Table 14. Properties of Products from Hydrogenation of Naphtha on Shell 424 Ni-Mo Catalyst--Process Conditions and Product Properties

	Product Number		
	123-106- 87-10-2	123-106- 87-10-4	123-106- 87-10-6
<u>Process Conditions</u>			
Pressure, psig	500	500	500
LHSV	1.0	1.0	1.0
Temperature, °F	400	450	500
Hydrogen Feed, scfb	1,500	1,500	1,500
H ₂ Consumption, scfb	270	430	660
<u>Product Properties</u>			
Specific Gravity, 60/60°F	0.826	0.816	0.806
Carbon, wt %	89.9	89.8	89.5
Hydrogen, wt %	9.8	10.1	10.3
Nitrogen, ppm	872	114	26
Sulfur, ppm	1,271	875	551
Oxygen, wt %	<0.1	<0.1	<0.1
<u>Hydrocarbon Composition, wt %</u>			
Monocycloalkanes	--	--	58.4
Benzene/Alkylbenzenes	--	--	41.6
<u>Distillation (ASTM D-2887)</u>			
IBP	74	67	66
5/10	126/156	106/137	91/121
20/30	168/176	164/172	161/169
40/50	186/210	181/195	178/188
60/70	225/231	221/228	214/227
80/90	252/283	237/276	233/273
95	341	302	287
FBP	725	641	597

possible BTX content in the product, which would maximize its value as either a petrochemical or a gasoline blending component.

These experiments demonstrate that the naphtha is easily upgraded, but the product is too low boiling to contribute significantly to jet fuel production.

SECTION IV

PREPARATION AND ANALYSIS OF TEST FUELS

1. PREPARATION OF JP-8 AND JP-8X

Calculated proportions of a blend of two intermediate products for distillation of a JP-8 test fuel were 77 vol % product 367-8-87-11-7 and 23 vol % product 367-8-87-11-4, which contained over 46 wt % aromatics. This blend minimized paraffins content while increasing the calculated aromatics content of the blend to 24.6 wt %. The intent was to reach 0.85 (JP-8X) density in a 230-600°F (110-316°C), distillate matching the ASTM D-2887 boiling range of a JP-8 fuel sample provided by WAL but limiting the aromatics content in the distillate to about 24 vol %.

An 8-liter blend of the calculated proportion was distilled in a Podbielniak Hypercal distillation unit equipped with a 5 1/2-ft column packed with stainless steel helipak. A distillate boiling in the range equivalent to 230-600°F (110-316°C) at 760 torr was collected at reflux ratio 10. The portion collected at vapor temperatures 230-400°F (110-204°C) was distilled at atmospheric pressure, and the remainder was distilled at a pressure of 10 torr. Distillate yield was 6,130 mL (76.6 vol %). Measured and calculated properties of the distillate, which are in good agreement, are found in Table 15. Distillate compositions are calculated from GC/MS analysis of the process intermediate and known boiling points of components. The density is slightly low for JP-8X, and paraffins content is much higher than the 10% target maximum. However, this product apparently meets critical requirements for grade JP-8 at very nearly the maximum specification density.

A second attempt was made to prepare a JP-8X product by reducing the distillate range to 300-600°F (149-316°C) while permitting up to 30 vol % aromatics content. Calculations showed that product 367-8-87-11-6 could yield a distillate of this narrower boiling range containing slightly more than 30 wt % aromatics, which corresponds to about 30 vol % aromatics. Distillation was conducted on this intermediate as previously described. The distillate fraction equivalent to the 300-600°F (149-316°C) boiling range at 760 torr was collected. Distillate yield was 75.4 vol % of the charge. Calculated and measured properties of the product are found in Table 16. Disparities between the measured and calculated contents of paraffins and dicycloalkanes are conspicuous, but the overall comparison for total saturates and aromatics is good. The measured values for hydrocarbon types are actually more favorable than expected because they are lower than those calculated for paraffins and higher for the denser dicycloalkanes, tricycloalkanes and indanes/tetralins. Although the density and hydrogen content exceed target JP-8X specification requirements, the freezing point is 25°F too high. This high freezing point was unexpected because of the relatively low paraffins content, since high paraffins content is frequently a cause of such a problem. We can only speculate that the combination of relatively low monocyclics concentrations with high-boiling paraffins may be responsible.

Table 15. Measured and Calculated Properties of 230-600°F
Distillate from a Blend of Hydrogenated Products
367-8-87-11-4 and 367-8-87-11-7

Properties	Measured	Calculated
Specific Gravity, 60/60°F	0.838	--
Hydrogen, wt %	13.6	13.4
<u>Hydrocarbon Composition</u>		
Paraffins, wt %	20.5	21.1
Monocycloalkanes	15.7	15.2
Dicycloalkanes	38.2	37.4
Tricycloalkanes	2.7	2.3
Total Saturates, wt %	77.1	76.0
Alkylbenzenes, wt %	12.2	13.0
Indanes/Tetralins	10.8	11.0
Total Aromatics	23.0	24.0
Yield, wt % of charge	82	86
Yield, vol % of charge	77	--
Freezing Point, °F	-60	--
Flash Point, °F	102	--
Viscosity at -4°F, cSt	4.11	--
<u>Distillation (ASTM D-2887)</u>		
IBP, °F	228	230
5/10	255/274	--
20/30	316/350	--
40/50	367/388	--
60/70	411/441	--
80/90	472/508	--
95	531	--
FBP	563	600

**Table 16. Measured and Calculated Properties of 300-600°F
Distillate from Hydrogenated Product 367-8-87-11-6**

<u>Properties</u>	<u>Measured</u>	<u>Calculated</u>
Specific Gravity, 60/60°F	0.856	--
Hydrogen Content, wt %	13.3	--
<u>Hydrocarbon Composition</u>		
Paraffins, wt %	6.3	15.3
Monocycloalkanes	7.9	8.4
Dicycloalkanes	46.8	41.0
Tricycloalkanes	5.3	3.0
Total Saturates, wt %	66.3	67.7
Alkylbenzenes, wt %	15.3	16.6
Indanes/Tetralins	18.4	15.7
Total Aromatics, wt %	33.7	32.3
Yield, wt % of charge	76.9	75.7
Yield, vol % of charge	75.4	--
Freezing Point, °F	-22	--
Viscosity at -4°F, cSt	7.36	--
<u>Distillation (ASTM D-2887)</u>		
IBP, °F	296	300
5/10	325/343	--
20/30	365/387	--
40/50	407/436	--
60/70	467/498	--
80/90	533/583	--
95	599	--
FBP	620	600

2. FUELS POTENTIAL OF TAR OIL HYDROGENATION PRODUCTS

One of the objects of this investigation was to evaluate intermediate hydrogenation products as sources for jet fuels. Most of the experimental effort was devoted to tar oil processing, since it seemed apparent at the outset that tar oil was the most promising source of jet fuels available from Great Plains by-products, based on relative production levels and by-product properties. Only a few of the tar oil

process intermediates proved to be worth considering as turbine fuel sources, and only two test fuels were produced, both of which are JP-8 types. A more complete evaluation was provided by calculating compositions for typical jet fuel distillates available from the three best process intermediates.

Calculated compositions based on GC/MS data for distillates corresponding to grades JP-4 (IBP-580°F [IBP-304°C]), JP-8 (230-600°F [110-316°C]), and a narrow-boiling JP-8X (300-600°F [149-316°C]) are found in Tables 17-19. Composition values in each table for IBP-900°F (IBP-482°C) are those measured by GC/MS for the whole intermediate product. The most notable trends in calculated compositions are the decrease in saturates and corresponding increase in aromatics as the initial boiling point of each distillate increases. Saturates decrease results from the loss of lower-boiling paraffins and cycloalkanes. Aromatics concentration increases as indanes/tetralins content increases while benzenes concentrations are about constant. These trends indicate that the density of jet fuel distillates should increase with increase in initial boiling point by exclusion of lower-boiling saturates. This in turn indicates that production of a high-density fuel from hydrogenated tar oil would require careful control of aromatics content at or near the 30% maximum and optimization of the initial boiling point in the 230-300°F (93-149°C) range. However, the freezing point adjustment may present a more difficult problem because of the presence of paraffins.

The intermediate hydrogenation products sufficiently saturated to be considered as turbine fuel sources contain 20-25 wt % paraffins. These are ubiquitous across the jet fuel boiling range and may precipitate from fuel mixtures at low temperatures. About two-thirds of these paraffins are created by ring opening during hydrogenation. Optimizing the process to minimize ring opening should improve the prospects for obtaining a higher density fuel with an acceptably low freeze point.

One intermediate product, 367-8-87-11-7, could have yielded either a JP-4 or a JP-8 distillate of acceptable quality (see Table 19). This is the most severely hydrogenated product produced in this investigation, representing a hydrogen consumption level of over 3,700 scfb. Product 367-8-87-11-6, from which a prototype JP-8X was distilled, could not have yielded a specification grade JP-4 or JP-8 because of high aromatics content, even though this product represents a hydrogen consumption level of more than 3,500 scfb.

Although these experiments were not intended to define optimum process conditions, they demonstrate that hydrogen requirements to produce any type of jet fuel from Great Plains by-product liquids suitable for use in present-day military aircraft will be extremely high.

Table 17. Composition of a Tar Oil Process Intermediate^a and Predicted Compositions and Yields of Its Distillate Fractions

Hydrocarbon Type	True Boiling Range, °F			
	IBP-900 (intermediate)	IBP-580 JP-4	230-600 JP-8	300-600 JP-8X
Paraffins, wt %	23.1	16.8	16.3	12.1
Monocycloalkanes	17.1	16.4	12.7	7.9
Dicycloalkanes	27.6	32.1	34.6	41.3
Tricycloalkanes	2.0	2.3	2.5	3.0
Total Saturates, wt %	69.8	66.6	66.1	64.3
Alkylbenzenes, wt %	17.1	17.8	18.3	17.0
Indanes/Tetralins	13.1	14.5	15.6	18.7
Naphthalenes	trace	trace	trace	trace
Total Aromatics, wt %	30.2	32.3	33.9	35.7
Yield, wt %	100.0	96.1	89.3	74.7

^a Product no. 367-8-87-5 from hydrogenation of raffinate-heavy distillate blend, 87-08-9. See Table 12 for process conditions.

Table 18. Composition of a Tar Oil Process Intermediate^a and Predicted Compositions and Yields of Its Distillate Fractions

Hydrocarbon Type	True Boiling Range, °F			
	IBP-900 (intermediate)	IBP-580 JP-4	230-600 JP-8	300-600 JP-8X
Paraffins, wt %	21.8	19.4	17.8	15.3
Monocycloalkanes	17.0	16.6	12.7	8.4
Dicycloalkanes	28.3	32.0	35.1	41.0
Tricycloalkanes	2.4	2.3	2.5	3.0
Total Saturates, wt %	69.5	70.3	68.2	67.7
Alkylbenzenes, wt %	17.8	17.5	18.4	16.6
Indanes/Tetralins	12.7	12.2	13.4	15.7
Total Aromatics, wt %	30.5	29.7	31.8	32.3
Yield, wt %	100.0	97.2	88.3	75.7

^a Product no. 367-8-87-11-6 from hydrogenation of raffinate-heavy distillate blend, 87-08-9. See Table 12 for process conditions.

**Table 19. Composition of a Tar Oil Process Intermediate^a
and Predicted Compositions and Yields of Its
Distillate Fractions**

Hydrocarbon Type	True Boiling Range, °F			
	IBP-900 (intermediate)	IBP-580 JP-4	230-600 JP-8	300-600 JP-8X
Paraffins, wt %	25.8	23.6	22.1	18.8
Monocycloalkanes	20.6	21.2	16.3	10.2
Dicycloalkanes	33.5	34.6	39.0	47.0
Tricycloalkanes	2.0	2.0	2.3	2.8
Total Saturates, wt %	81.9	81.4	79.7	78.8
Alkylbenzenes, wt %	9.5	9.8	10.3	9.3
Indanes/Tetralins	8.5	8.7	9.8	11.9
Total Aromatics, wt %	18.0	18.6	20.2	21.2
Yield, wt %	100.0	97.0	85.9	71.3

^a Product no. 367-8-87-11-7 from hydrogenation of raffinate-heavy distillate blend 87-08-9. See Table 12 for process conditions.

SECTION V

CONCLUSIONS

Tar oil is the only by-product with significant potential for jet fuels production. If a conventional fixed bed system is employed for hydroprocessing, the oil will probably require predistillation to remove particulate matter. Production of specification grade JP-4 or JP-8 from tar oil will probably require more than 3,400 scfb hydrogen. Production of JP-8X may require special processing and blending to achieve the desired density and avoid freeze point problems. Optimizing process conditions to minimize paraffins formation may be the critical step. Removing some oxygen compounds by extraction before hydroprocessing could improve process efficiency by conserving hydrogen.

Hydrogenation of the crude phenols by-product is a technically feasible but wasteful process. About 25% of the process hydrogen consumption is lost to water production. The hydrocarbon product is mostly low-boiling cyclohexanes and paraffins, which could make a minor contribution to production of JP-4 or JP-8.

The naphtha by-product has no potential for jet fuel production. After mild hydrodesulfurization, the product is a light gasoline with high BTX content that could be useful for gasoline blending. The process probably could be optimized to retain a higher BTX content than found in products generated in this work.

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